Translation

(12) International Application Published under the Patent Cooperation Treaty

(19) **World Intellectual Property Organization**, International Bureau

(10) **International Publication No.**

WO 02/26908 A1

(43) **International Publication Date**
4 April 2002

PCT

(51) **International Patent Classification**[7]:
C 09 J 11/04, 5/00, 175/04, B32B 7/12

(21) **International Application Number:** PCT/EP01/10808

(22) **International Filing Date:** 19 September 2001

(25) **Language of the International Application:** German

(26) **Language of the International Publication:** German

(30) **Priority Data:**
100 48 059.4 28 September 2000 DE

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(81) **Designated States (National):** AU, BG, BR, BY, CA, CN, CZ, DZ, HU, ID, IN, IS, JP, KR, MX, NO, NZ, PL, RO, RU, SG, SI, SK, UA, US, UZ, VN, YU, ZA.

(84) **Designated States (Regional):** European Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

Published:
— *With international search report*
— *Before expiration of the period allowed for amendments to the claims. Will be republished if amendments are submitted.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** ADHESIVES HAVING BARRIER PROPERTIES

(57) **Abstract**

Bonding agent-based compositions that contain filler that has a platelet-type crystallite structure and an aspect ratio > 100. Said compositions are suited for producing composite films and composite packaging materials that exhibit a good barrier effect against the diffusion of oxygen, aroma substances, and/or water vapor. Composite materials of this type are suited for the packaging of food products and medicines in order to protect them from the effect of oxygen or prevent aroma substances and/or water vapor from diffusing out.

"Adhesives having barrier properties"

This invention relates to an adhesive composition that exhibits barrier characteristics, to a method for producing composite films that exhibit a barrier effect, and to the use of said composite films for packaging.

For transport or storage, many goods require protection from the surrounding air or ambient atmosphere, and other goods, particularly those that have a high moisture content, must be protected from drying out. For this reason, such goods must be packaged in a manner suitable for excluding to the greatest extent possible all or certain constituents of the ambient atmosphere, or which prevents water or aroma substances from diffusing into the ambient atmosphere, and thus which prevents the packaged goods from drying out or undergoing an alteration in taste. A particularly critical constituent of the ambient atmosphere is oxygen, the presence of which in many packaged goods, such as food products or medicines, can lead to oxidative deterioration or to bacterial growth, which can also cause spoilage of the packaged goods.

Polymer films composed of thermoplastic films are widely used for the production of flexible packaging. These polymer films are usually produced using simple molding processes such as extrusion or blow molding.

Since the entire range of requirements imposed on modern packaging films cannot be satisfactorily met by a polymer film composed of a single polymer, production changed over some time ago to so-called composite films, i.e., films that have a multilayer structure. In order to achieve the essential basic properties of a packaging film, such as

resistance to tearing, taste neutrality, and barrier characteristics, three different methods are currently in use for bonding the individual film components to produce a composite film:

- Formation of multilayer systems having a separate barrier layer by combining polyvinylidene chloride films, ethylene–vinyl alcohol films, and/or aluminum foils with polyethylene films, polyester films, and/or polyvinyl chloride films. This multilayer system can be formed either by co-extrusion or by adhesive bonding of separately produced films.

- Vapor deposition of packaging films based on polyethylene terephthalate or biaxially oriented polypropylene, for example, with an aluminum oxide and/or silicon oxide layer under vacuum.

- Surface refinement of flexible packaging films by coating the films with solvent- or water-based polyvinylidene chloride solutions or dispersions, in some cases with the application of primer being necessary in a preceding process step to effect good adhesion of the surface coating to the substrate film.

WO 98/03332 describes a laminated packaging material for the production of heat-sealable packaging for liquid food products such as milk, cream, and juice. This multilayer laminate has a core layer of paper or cardboard: a polyethylene (low-density polyethylene or LDPE) layer is applied on one side, while the side facing the packaged material bears an oxygen- and aroma-proof barrier layer composed of ethylene–vinyl alcohol and polyamide. The ethylene–vinyl alcohol and polyamide layers must be joined directly and without adhesive, and their extrusion must be carried out in such a manner that these barrier layers are joined together in the molten state and this composite can

then be applied to the paper or cardboard core layer. WO 98/03332 also proposes that an additional LDPE layer be placed on this barrier layer using an adhesive. This manufacturing process is obviously very costly.

WO 97/42028 describes a multilayer metallized packaging film that has a core layer composed of polymer, for example, oriented polypropylene homopolymer (OPP), on at least one side of which there is applied a thin polymer layer that has a lower melting temperature than that of the core layer. The outwardly facing surface of the thin skin layer is then treated by flame or corona discharge to increase the adhesion to a subsequently applied metal layer, for example, aluminum. An additional polymer layer that is heat-sealable at low temperatures, such as ethylene–alkyl acrylate or methacrylate copolymer, is applied to this metal layer. The referenced document also proposes coating of the core layer with a vinylidene chloride copolymer component with the aid of a primer.

WO 97/30847 describes a multilayer packaging film that exhibits a barrier effect against oxygen migration. This thermoplastic multilayer packaging film has a core layer comprising an ethylene–vinyl alcohol copolymer film as its oxygen barrier, as well as two outer layers and two adhesive layers with the adhesive layers being positioned between the core layer and the two outer layers. At least one of the outer layers comprises a blend of three components, which may be homogeneous or heterogeneous, comprising an ethylene–α-olefin copolymer with a density between 0.195 [sic] g/cm^2 [sic] and 0.925 g/cm^2 [sic], a homogeneous or heterogeneous ethylene–α-olefin copolymer with a density ≥ 0.925 g/cm^2 [sic], and a homogeneous or heterogeneous ethylene–α-olefin copolymer with a density ≤ 0.915 g/cm^2 [sic]. The referenced document also discloses that in preferred embodiments the multilayer laminate can have additional layers between the adhesive layers and the outer layers.

Thus, for example, six- or preferably seven-layer films can be produced, and the additional layers can be either recycled material or other polymer films such as, for example, polyamide films.

Japanese Laid Open (Unexamined or Kokai) Patent Application Number Hei 06-048474 A2 describes an oxygen-impermeable thermoplastic composite film for packaging food products. This laminate comprises a core film, an oxygen barrier layer, an adhesive layer, and a layer of a thermoplastic resin that contains a metal compound. A cobalt stearate-containing polypropylene is recommended as the metal compound-containing layer. These two polypropylene layers are bonded to a layer of polyvinylidene chloride using a polyurethane adhesive.

Japanese Laid Open (Unexamined or Kokai) Patent Application Number Sho 63-132049 A describes laminates comprising a core layer of an ethylene–vinyl alcohol copolymer or a polyvinyl alcohol layer, which is laminated on both sides with a polypropylene layer containing 10 to 70% mica, talc, or calcium carbonate. This composite film is reported to have a good oxygen barrier effect and good bending resistance.

Japanese Laid Open (Unexamined or Kokai) Patent Application Number Hei 09-234811 A describes films and sheets that are suitable for storing food products, medicines, or metals and that prevent oxidation of the packaged goods. These films are formed from a microporous layer which typically contains antioxidant [sic, this should be deoxidant here and in the following reference to an "antioxidant-containing layer" — Translator], a nonporous oxygen-permeable thermoplastic layer, and a microporous oxygen-permeable thermoplastic layer that contains water-insoluble particles, and optional

additional layers. The antioxidant-containing layer is laminated on both sides with the other thermoplastic layers, wherein these are melt-bonded to each other.

WO 97/123350 [sic, this should probably be WO 97/23350 — Translator] describes polymer films comprising at least one layer of a thermoplastic polymer to which a layer comprising a filler in a dispersant is applied. The particle-like filler preferably has a lamellar structure, and the dispersant should contain a tackifying resin. The filler dispersion may form an outer layer or an inner layer of the film. According to the teaching of this document, such films exhibit good barrier effects against oxygen and other gases, and it is proposed that the films be used for packaging plant materials such as hay and straw.

The structures heretofore known in the art for good-barrier composite packaging materials are costly to produce. The use of metal layers, either by metal vapor deposition or by metal film lamination, in practice always results in flaws from numerous small holes in the metal layer that significantly impair the otherwise good barrier characteristics of metal layers.

In light of this prior art, the object of this invention is to provide a simple method for producing composite materials of plastic films wherein said composite materials exhibit very good barrier characteristics, in particular against oxygen, aroma substances, and water vapor.

As described in the claims, the object of this invention is achieved essentially by providing lamination adhesive compositions that are based on a polymer bonding agent and that contain filler that has a platelet-type crystallite structure and an aspect ratio > 100.

Additional subject matter of the present invention is the introduction of a method for producing composite films that comprise at least two identical or different plastic films that are bonded together by a lamination adhesive that contains filler that has a platelet-type structure and an aspect ratio > 100. Other subject matter of the present invention relates to the use of the composite films thus produced for the packaging of food products and medicines.

The direct use in the production of composite materials of an adhesive — which in addition to adhesive bonding of the films also results in an active barrier against lower molecular weight compounds such as gases, water vapor, and aroma substances — has many advantages:

Lamination of the packaging composite to achieve taste neutrality and printability as well as to impart barrier characteristics can be performed in one process step. Additional coatings with polyvinylidene chloride and/or ethylene–vinyl alcohol layers, or vapor deposition with an aluminum layer, are not necessary. Thus, the number of production steps is decreased and the cost-effectiveness ratio of the packaging material is improved. The absence of a metal layer enables greater type purity and therefore less expensive disposal of these packaging composites.

The filler having a platelet-type crystallite structure and an aspect ratio > 100 will generally have a thickness of only a few nm, but the length or width of the crystallite can be up to several µm. Such fillers are also referred to as "nanoparticles." The formation of labyrinthine structures from the filler in the polymer adhesive matrix lengthens the diffusion path of low molecular weight compounds such as, for example, oxygen, water, carbon dioxide, and aroma and/or flavor substances, in such a way that their migration

through the adhesive layer is drastically reduced or, in the ideal case, completely prevented.

Suitable compounds for these fillers are the oxides, hydroxides, nitrides, halides, carbides, and mixed oxide/hydroxide/halide compounds of aluminum, silicon, zirconium, titanium, tin, zinc, iron, alkali metals, and alkaline earth metals. These are principally clays such as aluminum oxides, boehmite, bayerite, gibbsite, diaspore, and the like. Particularly preferred are phyllosilicates such as bentonite, montmorillonite, hydrotalcite, hectorite, kaolinite, boehmite, mica, vermiculite, and their mixtures. These fillers can be subjected to surface modification with organic compounds to improve filler dispersibility in the bonding agent matrix.

Bonding agents suitable for these lamination adhesive compositions and as the dispersion medium for the filler encompass all generally known one- and two-component lamination adhesive bonding agents such as hot-melt adhesives and polyurethane-based reactive hot-melt adhesives, particularly preferably one- and two-component reactive polyurethane adhesives.

The reactive one-component polyurethane adhesives can be moisture-curing adhesives in the form of either liquids or pastes, but can also be reactive hot-melt adhesives. Particularly preferred, however, are room temperature-curable two-component adhesives in which one component is hydroxyl-functional prepolymer and the second component is a higher molecular weight low-volatility polyisocyanate. The composition of such lamination adhesives is described in detail in, for example, DE 3401129 A, DE 44417705 A, DE 19754926 A, and DE 19832556 A. The therein described polyurethane bonding agents for lamination adhesives are expressly included as part of the present application.

The inventive adhesives which exhibit a barrier effect are suitable for laminating a wide variety of composite films, i.e., for bonding various plastic films to one another and/or to paper webs. The plastic films may be composed of any of the common plastics used for film production, such as, for example, polyethylene, polypropylene and particularly oriented polypropylene (OPP) produced by mono- or biaxial stretching, polyester and particularly polyethylene terephthalate (PET), PVC, polyamide, and polyimide. The paper webs and plastic films may be coated or printed. Another application for the inventive adhesives is the production of bags from blow-molded or woven polyethylene or polypropylene tubes.

The inventive adhesives may be applied to the substrates to be adhesively bonded using any common application method.

The invention is described in greater detail below with reference to several preferred exemplary embodiments, but the choice of examples does not limit the scope of the subject matter of this invention. Unless specified otherwise, all quantities in the following examples are weight percent or parts by weight relative to the total composition, or, for two-component adhesives, relative to the individual components.

Examples

In the following examples, two-component polyurethane adhesives commercially available from Henkel were modified with filler whose use is taught by this invention. To this end, the filler was dispersed in the hydroxyl-functional component (Liofol UR 8155 or UR 8156) of the polyurethane adhesive using an ultrasound dispergator or a high-speed Ultra Turrax mixer. Desmodur N 3300 or Desmodur VP 8712 (Bayer) was used

as the isocyanate component. The quantitative proportion of the Liofol component to the isocyanate component was chosen in keeping with the manufacturer's recommendation. Two OPP films were adhesively bonded together and the oxygen transmission rate (OTR) and water vapor transmission rate (WTR) were measured after the adhesive had cured. The effective barrier activity was determined in relation to the OPP composite that was adhesively bonded using the unfilled lamination adhesive with the same composition. As can be seen from the examples in the following table, all lamination adhesives modified in accordance with this invention showed a significant reduction in the oxygen transmission rate.

Table 1.

example	OH component	nanoparticle 1)	filling level 2) wt%	viscosity 3) mPa·s 25°C	viscosity 3) mPa·s 40°C	dispersing method	composite/OTR/comments 4)	Eff. 5)
1	Liofol UR 8156 comparative	—	—				OPP/OPP, Desmodur N3300 eff. filler content: 0.0% OTR: 1480 (1870)	—
2	Liofol UR 8155	EX 0032	10	16500	6260	2.5 min ultrasound	OPP/OPP, Desmodur N3300 eff. filler content: 5.9% OTR: 1140	-23%
3	Liofol UR 8155	EXM 804	10	6680	2310	30 s Ultra Turrax	Desmodur VP 8712 eff. filler content: 4.6% OTR: 190, WTR: 296	-49%
4	Liofol UR 8156	EX 0032	10	16700	5820	2.5 min ultrasound	OPP/OPP, Desmodur N3300 eff. filler content: 5.9% OTR: 1080	-27%
5	Liofol UR 8156	hectorite/benzyl-dimethyl(2-hydroxy-ethyl)ammonium	10	5800	1800	1.5 min Ultra Turrax, 2.5 min ultrasound	OPP/OPP, Desmodur N3300 eff. filler content: 5.9% OTR: 954	-35%
6	Liofol UR 8156	hectorite/dodecyl-ammonium	10	5800	1900	1.5 min Ultra Turrax, 2.5 min ultrasound	OPP/OPP, Desmodur N3300 eff. filler content: 5.9% OTR: 853	-42%
7	Liofol UR 8156	hectorite/Dehyquart L80	10	5000	1700	1.5 min Ultra Turrax, 2.5 min ultrasound	OPP/OPP, Desmodur N3300 eff. filler content: 5.9% OTR: 719	-52%

example	OH component	nanoparticle 1)	filling level 2) wt%	viscosity 3) mPa·s 25°C	viscosity 3) mPa·s 40°C	dispersing method	composite/OTR/comments 4)	Eff. 5)
8	Liofol UR 8156	Somasif/dodecyl-ammonium	10	8200	2800	1.5 min Ultra Turrax, 2.5 min ultrasound	OPP/OPP, Desmodur N3300 eff. filler content: 5.9% OTR: 949	-36%
9	Liofol UR 8156	Somasif/benzyl-dimethyl(2-hydroxy-ethyl)ammonium	10	4900	1600	1.5 min Ultra Turrax, 2.5 min ultrasound	OPP/OPP, Desmodur N3300 eff. filler content: 5.9% OTR: 1237	-16%
10	Liofol UR 8156	Somasif/Dehyquart L80	10	5000	1500	1.5 min Ultra Turrax, 2.5 min ultrasound	OPP/OPP, Desmodur N3300 eff. filler content: 5.9% OTR: 764	-48%
11	Liofol UR 8156	Somasif/1,12-diaminododecane	10	5400	1800	1.5 min Ultra Turrax, 2.5 min ultrasound	OPP/OPP, Desmodur N3300 eff. filler content: 5.9% OTR: 667	-55%
12	Liofol UR 8156	Nano 2124	10			sand-colored, uniformly free-flowing	OPP/OPP, Desmodur N3300 eff. filler content: 5.9% OTR: 1060, WTR: 0.91	-28%

Notes

1) See Table 2 for an explanation of the fillers (nanoparticles)
2) Filler content relative to the Liofol UR component
3) Thermocel viscosimeter by Brookfield
4) OPP = oriented polypropylene, eff. filler content = effective content of filler relative to the overall adhesive composition
5) Efficacy, i.e., reduction in OTR relative to the unfilled comparative example

Table 2: Fillers Used

filler/modifier	producer	modifier
EX 0032, montmorillonite	Süd-Chemie	C_{18} n-alkyl/benzyl
EXM 804, montmorillonite	Süd-Chemie	terminal OH groups
Somasif, sodium magnesium fluorosilicate	Co-op Chemical Co., Ltd., Japan	
Dehyquart L80	Henkel	bis(cocoyl)ethylhydroxyethylmethylammonium Methosulfate
Nano 2124, montmorillonite	Nanocor	n-dodecylpyrrolidone

Claims

1. Lamination adhesive composition based on a polymer bonding agent, characterized in that it contains filler having a platelet-type crystallite structure with an aspect ratio > 100.

2. Lamination adhesive composition according to Claim 1, characterized in that the effective filler content of the filler in the bonding agent matrix is 0.1 to 30 weight% and preferably 5 to 15 weight%.

3. Lamination adhesive composition according to Claim 1 or 2, characterized in that the filler is selected from the oxides, hydroxides, nitrides, halides, carbides, and mixed oxide/hydroxide/halide compounds of aluminum, silicon, zirconium, titanium, tin, zinc, iron, alkali metals, and alkaline earth metals.

4. Lamination adhesive composition according to Claim 3, characterized in that the filler is selected from the group comprising aluminum oxide, boehmite, bayerite, gibbsite, diaspore, bentonite, montmorillonite, hydrotalcite, hectorite, kaolinite, mica, vermiculite, and their mixtures.

5. Lamination adhesive composition, characterized in that a one- or two-component polyurethane adhesive is used as the bonding agent.

6. Lamination adhesive composition according to Claim 5, characterized in that one component of the bonding agent system contains hydroxyl-functional polymer and the filler and the second component contains polyisocyanate as curing agent.

7. Method for producing composite films comprising at least two identical or different plastic films, characterized in that a composition according to Claims 1 through 6 is used as the lamination adhesive.

8. Composite film produced according to Claim 7, characterized by its barrier activity against the diffusion of oxygen, aroma substances, and/or water vapor.

9. Use of a composite film according to Claim 8 for the packaging of food products or medicines.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/10808

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09J11/04 C09J5/00 C09J175/04 B32B7/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09J B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 97 23350 A (SHIMELL RICHARD JOHN) 3 July 1997 (1997-07-03) cited in the application claims 1-5,16-19,28 page 4, paragraph 3 -page 5, paragraph 1 page 9, paragraph 4 -page 10, paragraph 2	1-4,7-9
Y	EP 0 301 878 A (DU PONT) 1 February 1989 (1989-02-01) claims 1,9,16 column 2, line 4 - line 11 column 4, line 35 -column 5, line 9	1-4,7-9

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search	Date of mailing of the international search report
4 March 2002	12/03/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Schlicke, B

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Int ›nal Application No
PCT/EP 01/10808

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 03, 31 March 1999 (1999-03-31) & JP 10 338855 A (SUMITOMO RUBBER IND LTD), 22 December 1998 (1998-12-22) abstract	1-3
P,X	DE 199 60 411 A (DUPONT PERFORMANCE COATINGS GM) 5 July 2001 (2001-07-05) claims column 1, line 60 - line 31	1-9
E	WO 01 87566 A (TOURNIER SANDRINE ;FILLON BERTRAND (FR); LERDA JEAN JACQUES (FR);) 22 November 2001 (2001-11-22) claims 1,3,16,17 page 6, line 2 - line 10 page 15, line 8 - line 13	1-5,7-9
A	DE 299 20 721 U (WEISS CHEMIE & TECHNIK GMBH &) 9 March 2000 (2000-03-09) claim 1	1-9

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Additional matter PCT/ISA/210

International application No.
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Continuation of Field I.2

Claim No. 5 is formulated as a main claim, and Claim No. 6 is formulated such that it is dependent thereon. Since this is attributed, with a high probability, to an oversight and, furthermore, these claims in this formulation find no support in the description, no search was carried out for the subject matter resulting from this formulation.

The subject matter of the search is such that Claim No. 5 is dependent on Claims Nos. 1-4 and Claim No. 6 is dependent on Claim No. 6.

INTERNATIONAL SEARCH REPORT

formation on patent family members

Int[illegible]nal Application No
PCT/EP 01/10808

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